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## III.B.2 Development of Ni-Based Sulfur-Resistant Catalyst for Diesel Reforming

### Objectives

- Reform a real diesel fuel containing 50 parts per million sulfur under minimum recycle conditions using a low-cost (hence nickel-based) sulfur resistant catalyst to produce hydrogen and carbon monoxide for use in solid oxide fuel cells.
- Determine conditions that cause catalyst deactivation and ascertain the effectiveness of radio frequency coke suppression in prolonging catalyst activity.
- Measure the effect of frequency and field strength of the applied radio frequency field on suppressing coking of sulfur resistant reforming catalyst.

### Accomplishments

- Demonstrated that a low-cost nickel-based catalyst can autothermally reform a 50 ppm S diesel fuel with 20% recycle gas for at least 500 hours without catalyst deactivation, which is a major step towards developing a 5,000 to 10,000 hour stable reforming catalyst.
- Determined that coking is the major form of catalyst deactivation and can be controlled through proper catalyst formulation, introduction of turbulence into the flame front, and by possible application of radio frequency coke suppression.
- Determined that the radio frequency coke suppression effect appears to be linearly dependant upon field strength but is independent of frequency between 50 kHz to 13.56 MHz.

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### Introduction

For diesel, jet or gasoline to be used in a fuel cell, the liquid hydrocarbon fuel must first be reformed

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into hydrogen and carbon monoxide. Typically, the hydrocarbon fuel is first mixed with a limited amount of air, and in some systems a small amount of off-gases from the anode of the fuel cell stack to supply steam. The resulting mixture is then passed over a nickel or platinum group metal catalyst to produce hydrogen and carbon monoxide, which are then sent to the fuel cell stack to produce electricity. Reformer catalysts based on low-cost nickel are preferred, because they are cheaper to manufacture and more durable than platinum group metal catalysts. Unfortunately, even sub part per million levels of sulfur in the fuel can poison most reformer catalysts, resulting in a product stream with a high concentration of partially reformed hydrocarbons that will coke or foul the anode catalysts used in solid oxide or other type of fuel cell stack.

Chevron, Argonne National Laboratory, and the National Energy Technology Laboratory at Morgantown are developing Ni-based (low-cost) reforming catalysts that can tolerate the levels of sulfur found in reformulated gasoline or in low sulfur diesel fuel. Developing a sulfur resistant reforming catalyst is a far better approach than trying to adsorb complex sulfur compounds found in the fuel in a separate system prior to reforming, since most adsorbents for branched dibenzothiophenes have low capacities and are often pyrophoric.

### Approach

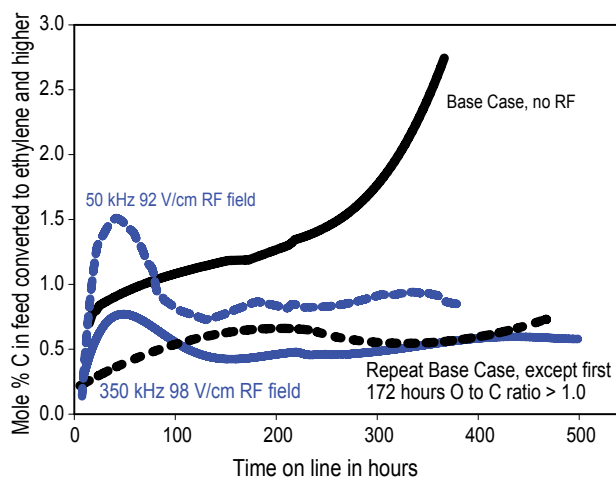
We have found that the most serious problem with the development of a sulfur resistant reforming catalyst is coking, and that Ni-based catalysts tend to coke more than platinum group metal based catalysts. However, Ni-based catalysts are preferred not only because they are significantly cheaper, but they are also more durable. Both of these issues are critical in ultimately developing a viable low-cost auxiliary power unit for less than \$400/kW. Not only does coke block catalytic sites leading to the production of undesirable heavy hydrocarbons that will foul anode catalysts, we have also found that coking leads to aging of the reformer catalyst due to metal stripping. Another problem with both platinum group metal and Ni-based reformer catalyst is that they require periodic regenerations every 8 to 100 hours or so to remove built-up carbon deposits. This can be easily accomplished when the auxiliary power unit is turned off, simply by stopping the flow of hydrocarbon feed over the catalyst before cutting off the flow of air. Normally, the coke on the catalyst is burned off in 1 to 3 minutes. The Chevron catalyst is formulated to remain active following air regenerations.

We tested the Chevron catalyst under autothermal reforming conditions first with a simulated recycle rate of 20% at an oxygen to carbon mole ratio of 1.0 with a steam to carbon mole ratio of 0.2. The purpose of the recycle stream from the SOFC anode is to provide a source of steam to prevent coking. However, late in the project we discovered that it was possible to operate the reformer with just air and diesel fuel alone, particularly if severe turbulence is deliberately introduced into the flame front. This can be achieved by reactor/catalyst geometry and space velocity or by “chopping” or “pulsing” the air supply. The majority of this project was focused on understanding the role radio frequency coke suppression plays in suppressing metal catalyzed coking and thus decrease reformer catalyst deactivation.

## Results

We have demonstrated that a 50 ppm S diesel fuel can be autothermally reformed to produce hydrogen and carbon monoxide for use in a solid oxide fuel cell over a low-cost Ni-based catalyst for more than 500 hours with no major sign of catalyst deactivation provided that (1) the catalyst is reformulated to avoid free surface Ni, and/or (2) radio frequency (RF) coke suppression is applied. Figure 1 shows the activity of the catalyst reforming a 50 ppm S diesel fuel as a function of time. In the base case, the activity of the catalyst rapidly decreased after approximately 200 hours due to excessive coking. When a radio frequency field of 50 kHz at 92 V/cm or 350 kHz at 98 V/cm is applied to the catalyst, the coking rates of the catalyst is substantially reduced in these runs. Without RF, the catalyst would require a periodic regeneration or a burn lasting 20 to 30 minutes (under the same flow of air used to reform the fuel); yet under RF coke suppression, the catalyst was regenerated in 5 to 8 minutes for a 10-hour run. Thus, application of a radio frequency electromagnetic field reduced coking by a factor of approximately 4. As a consequence, catalyst activity was stabilized for at least 500 hours. Since the coking rate of diesel drops dramatically with sulfur content and that diesel fuels in Europe and the United States will contain less than 15 ppm sulfur, we anticipate that this catalyst should survive substantially longer than in these “rapid” aging trials.

In Figure 1, we also see in the RF runs that the activity of the catalyst first decreases and then improves before lining out after approximately 125 hours on line. This activation of the catalyst is due to the reaction of “free” Ni or NiO on the surface with the underlying support. The original Ni-based catalyst was formulated to leave “green” free NiO on the surface. It was thought that this “free” nickel on the surface would adsorb sulfur in the front part of the catalyst bed, thereby allowing the back part of the catalyst bed to steam reform the fuel. However, we quickly discovered that the sulfur resistant



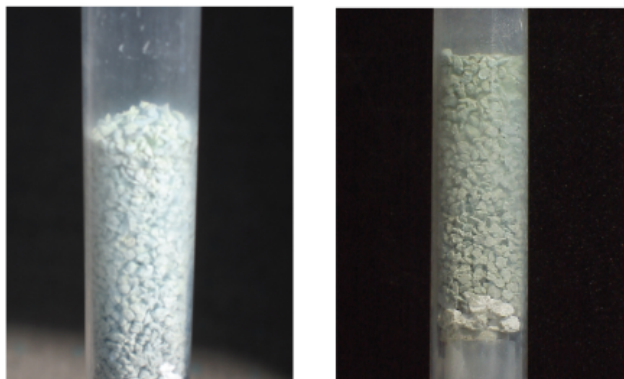
**FIGURE 1.** Catalytic Activity and Aging of Chevron’s Ni-based Catalyst Reforming a 50 ppm S Diesel Fuel with and without Radio Frequency Coke Suppression

reforming activity continued long after the catalyst quit adsorbing sulfur. Thus, we discovered that the sulfur resistance is due to the incorporation of nickel into the support to produce a blue colored catalyst of  $\text{Ni}^{+3}$  in an octahedral site. In fact, this is the same mechanism of sulfur resistance first proposed by Michael Krumpelt at Argonne National Laboratory in their perovskite based catalysts [1,2], and also imparts the sulfur resistance to the “hexaaluminate” series of catalysts being developed by David Berry and co-workers at the National Energy Technology Laboratory at Morgantown, WV [3]. Thus, in the “RF-on runs”, a portion of the Ni on the surface dissolves into the support to develop the sulfur resistance of the catalyst, which is seen as a gradual increase in catalytic activity over time in the first 125 hours.

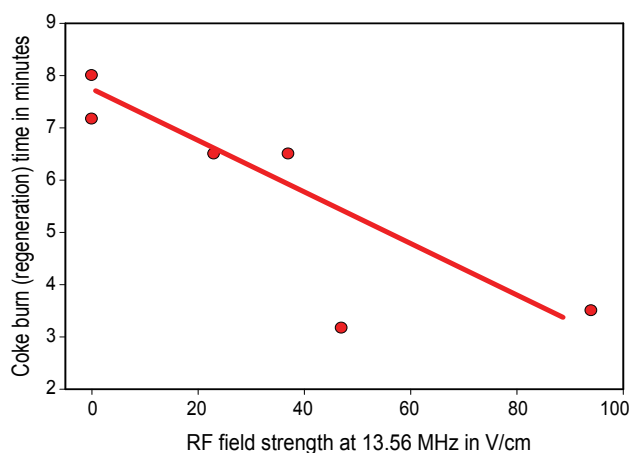
However, we also discovered that if the catalyst is either calcined at a higher temperature during preparation or as we serendipitously discovered that if the catalyst is run at an O to C ratio higher than 1.0 for even a short period of time, then the coking rate can be reduced to the same level as was seen in the RF coke suppression runs. By operating at a higher O to C ratio (of 1.1), the higher temperature drives the entire free surface Ni into the structure to produce a lower coking catalyst. This first occurred quite by accident during the repeat base case run in Figure 1 (dotted black line). As a result of a crack in the central quartz RF antenna well, extra air was pulled into the reactor for the first 172 hours because the test apparatus was under a slight vacuum. As a result of the higher temperature, the catalyst turned blue. However quite surprisingly, even after the quartz reactor was repaired, this modified catalyst now showed no signs of catalyst deactivation even though no RF was applied, and had the same low coking rate as occurred under RF coke suppression.

Aged catalyst from Figure 1 with no RF Coke suppression showing blue color of Ni+3 incorporated into the support.

Aged catalyst under 50 kHz RF showing green color of Ni+2 on the surface



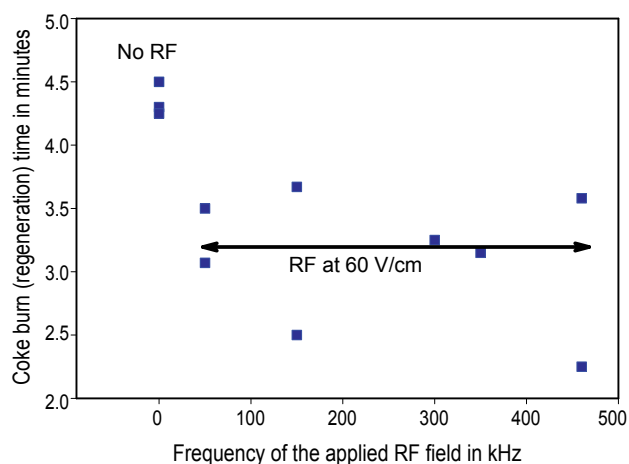
**FIGURE 2.** Comparison of Chevron's Ni-based Catalysts at the End of Run, Showing that RF Maintains the "Green" Color of Supported NiO (right), While the Base Case Is Blue Due to Incorporation of Ni into the Structure (left)



**FIGURE 3.** Effect of the RF Field Strength on the Coking Rate of the Catalyst

Clearly, if the catalyst is formulated and heat treated so that no free Ni remains on the surface, the coking rate on the catalyst can be reduced by a factor of approximately 4. Figure 2 compares the color of the two catalyst beds showing that RF coke suppression prevents nickel stripping. Thus, after 380 hours on line, the catalyst is still green due to supported NiO, whereas in the repeat RF off case (due to extra air in the beginning) the catalyst is blue.

Figures 3 and 4 show the effect of field strength (at 13.56 MHz) and frequency (at 60 V/cm field strength) on coking rate of the reforming catalyst. Figure 3 shows that the coking rate decreases linearly with increasing field strength, whereas Figure 4 quite surprisingly shows



**FIGURE 4.** Effect of Frequency on the Coking Rate of the Catalyst

that varying frequency over a range of 50 to 460 kHz has no impact on coking rate. In subsequent experiments covered in the final report, the RF coke suppression effect is shown to be independent of frequency over the range of 50 to 13.56 MHz [4].

Finally, we discovered that diesel fuel could be reformed over the catalyst with no additional steam if the oxygen to carbon mole ratio was increased to 1.1. Furthermore, it was subsequently discovered that the coking rate could be substantially reduced under the higher O to C mole ratio conditions to extremely low levels, if turbulence is introduced into the flame front. This was achieved again, quite serendipitously, by an inadvertent arrangement of reactor geometry and gas space velocity, which caused the flame front to rapidly pulsate. As a result, the coking rate dropped by a factor of 4. In the "real" world, the same effect can be obtained if the air supply would be pulsed to create local environments where the O to C mole ratio would change from about 1.0 to 1.2. When turbulence was used to reduce coking, RF coke suppression reduced coking only an additional 20%. Thus, turbulence is a better tool to suppress coking than is RF coke suppression.

## Conclusions and Future Directions

It was demonstrated that a low-cost Ni-based catalyst can reform a 50 ppm S containing diesel fuel with or without recycle gas. In addition, if coking on the catalyst is controlled by proper catalyst formulation, introduction of turbulence into the flame front, and by possible application of a RF electromagnetic field, catalyst deactivation can be avoided for at least 500 hours of operation. This is a good step towards developing a long term stable catalyst capable of reforming ultra low sulfur diesel fuel for at least 5,000 to 10,000 hours.

## **FY 2006 Publications/Presentations**

1. "Development of Ni-based Sulfur Resistant Catalyst for Diesel Reforming" Final Technical Progress Report, Gunther Dieckmann, May 18, 2006.

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3. "Hexaaluminate Catalyst Development", David Berry, 2005 SECA Core Technology Peer Review Workshop, Tampa, FL, January 27, 2005.
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